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FÜR MINERALÖL- UND KOHLEFORSCHUNG  
DER TECHNISCHEN HOCHSCHULE KARLSRUHE

January 3, 1963

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AS AD 404181

European Research Office (9851 DU)  
US Department of the Army  
Frankfurt/Main, Germany  
APO 757, US Forces

### FINAL TECHNICAL REPORT

Subject of the research:	Catalytic Isomerization of Paraffin base hydrocarbons with dual function metal catalysts in the field of diesel and jet fuels
Name of Contractor:	Prof. Dr. Helmut Pichler
Contract Number:	DA-91-591-EUC-2064
Type and number of report:	Final Technical Report No. 1
Period covered by report:	1. 12. 1961 - 30. 11. 1962

The research reported in this document has been made possible through the support and sponsorship of the U. S. Department of Army, through its European Research Office.

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### Abstract

The investigations on the isomerization and hydrocracking in the field of diesel and jet fuels were continued. Thus, with a soft paraffin wax as feed attempts have been made to obtain products with properties similar to diesel and jet fuels. The catalyst used was 0.1 wt. % Pd on alumina-boria (4:1), as it gave the best isomerization results with n-hexane as starting material.

In the case of experimental runs with the paraffin wax difficulties were encountered in the analysis of the reaction products. Their characterization was limited on the determination of some physical constants (e.g. cloud point, boiling range etc.) rather than on an investigation by gas chromatography. Thus a 10°C lowering of the cloud point between the feed and the product with the same initial boiling point was obtained.

The difficulties encountered in the analysis of the reaction products when high molecular weight hydrocarbons ( $C_{12}$  and higher) were used as the feed material indicated that it is better to carry out further studies with a lower hydrocarbon and as such n-nonane was selected as the feed material. The fewer number of possible isomers gives the possibility of identifying individual components and the experience obtained could be profitably used for the higher range of compounds.

As analytical tool gas chromatography in combination with mass spectrometry has been used.

Retention volumes of a large number of test substances (mostly C-9 isomers) were determined. By the use of two columns (silicone oil - 7.8-benzoquinoline) a better resolution of peaks consisting of more than one component has been attempted, so that characterization of the resolved peaks by mass spectrometry is facilitated.

Experimental runs with n-nonane were conducted both in batch and continuous operations. The maximum yield of C-9 isomers was obtained in the case of batch operations at a reaction temperature of 375°C and at a reaction time of 20 hours (apprxm. 45 wt. % of the liquid reaction product) and in the case of continuous operations at 425°C and 10 sec. reaction time (apprxm. 47 wt. % of the liquid reaction product).

The greater portion of C-9 isomers consisted of monomethyl isomers (over 65 wt. %). From the monomethylisomers it has been possible to identify the 2- 3- and 4-methyloctanes. From the dialkylisomers in the reaction product the presence of 2, 3 dimethyl-, 2, 5-dimethylheptane and 2-methyl 3-ethylhexane could be confirmed.

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## 1. Isomerization of n-Hexane

### The influence of Palladium content on the activity and selectivity of an aluminium-oxide carrier

In the Final Technical Report of the last year (Nov. 30, 1961, p. 15) it was stated that investigations of the influence of Palladium content on the activity and selectivity of an aluminium-oxide carrier have showed that high activity of the catalysts lies in the range of palladium contents between 0,1 - 0,5 wt. %.

The detailed results of these investigations are given here.

#### 1.1 Apparatus used

The experimental runs described were conducted with a flow type micro scale reactor allowing to work with small amounts of catalyst. The inner diameter of the reactor tube was 7,4 mm, the volume of the catalyst used for all the series of investigation 2 ml.

A Perkin Elmer Fractometer had been hooked up with the apparatus in such a way that samples of the reaction products could be drawn in for analysis at any desired time.

#### 1.2 Preparation of catalysts

To the acid solution of aluminium nitrate (E. Merck Nr. 1086) ammonia (E. Merck Nr. 5422) was added under vigorous stirring until a complete precipitation of the hydroxide was achieved. After filtration the precipitate was dried at 120°C for 12 hours and activated at 500°C for 3 hours.

For the impregnation with the Palladium-chloride solution particles of size 0,3 - 0,5 mm were selected. After the reduction at 500°C the catalysts showed the following surfaces:

$\text{Al}_2\text{O}_3$ - carrier without Pd	: 236 $\text{m}^2/\text{gr}$
" " with 0,02 % wt. Pd.	: 229 "
" " " 0,06 % " "	: 226 "
" " " 0,1 % " "	: 219 "
" " " 0,5 % " "	: 209 "
" " " 10 % " "	: 203 "

### 1.3 Reaction conditions

The experiments were conducted at different temperatures the other operating conditions being constant.

Temperatures: 350°C, 375°C, 400°C, 425°C, 450°C, 475°C

(Pressure 25 atm; liquid hourly space velocity 2 vol. /vol. /hour; mol. ratio  $\text{H}_2/\text{HC} = 2,5$ )

As feed normal hexane was used.

### 1.4 Results and discussion

The yield of the branched hexanes has been plotted in Fig. 1 against the reaction temperatures.

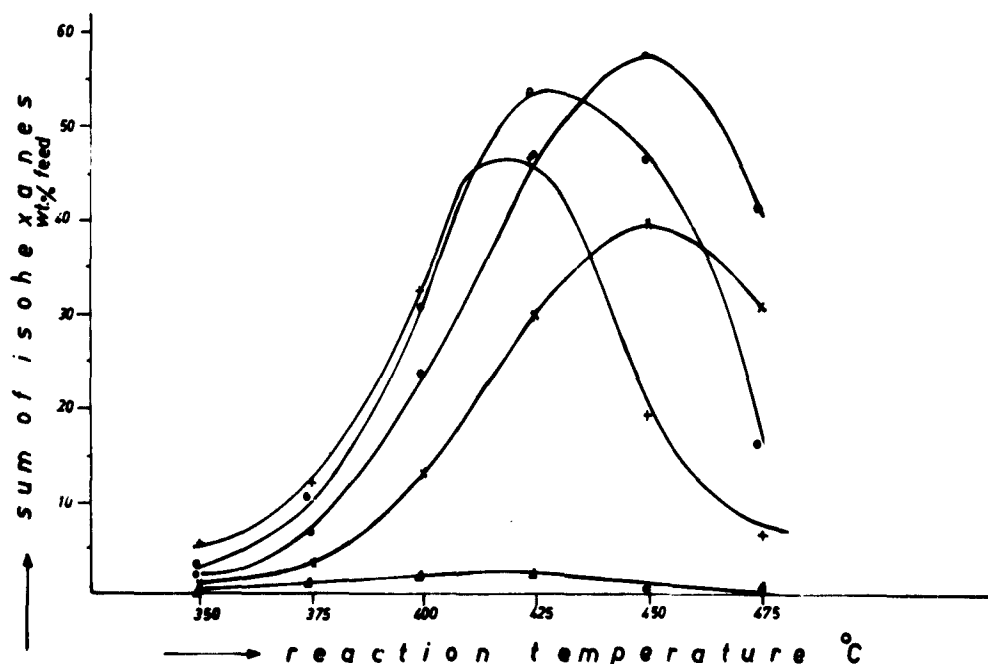


Fig. 1 Dependence of isohexanes-yield on reaction temperature for catalysts with various Pd-contents

▲	Al <sub>2</sub> O <sub>3</sub> -carrier with 0,02 % Pd
×	" " " 0,06 "
●	" " " 0,1 "
○	" " " 0,5 "
†	" " " 10 "

From this figure it can be seen that the rise in the Pd-content of the Al<sub>2</sub>O<sub>3</sub>-support from 0,02 to 10 wt. % caused the initiating of the isomerization reaction at lower temperatures. The differences in the yield of the branched hexanes at the lower concentrations of Palladium - 0,02, 0,06, 0,1, 0,5 wt. % - were relatively large. By a 20 fold increase in the concentration of the Palladium (10 wt. %) a considerable increase of the branched hexanes yield could not be achieved.

The yield-maximum is shifted to higher temperatures by decreasing the content of Palladium from 0,5 wt. % to lower values. The greatest isomer-yield was obtained with the catalyst containing 0,1 wt. % Pd. At lower concentrations of Palladium the activity of the catalyst was decreased very strongly, e.g. with a catalyst having a Pd-content of 0,02 wt. % only 2,5 wt. % of normal hexane was isomerized.

The extent to which the various catalysts affected the isomerization in connection with the cracking of normal hexane can be discussed on the basis of Fig. 2. In this figure the sum of cracked products has been plotted against the conversion.



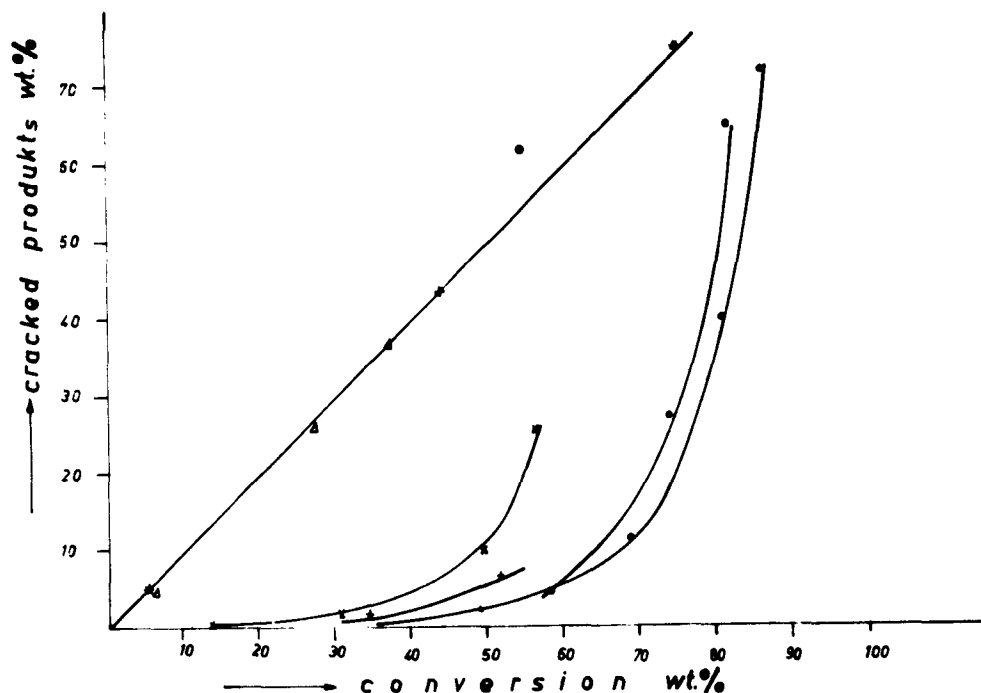


Fig. 2 Dependence of cracked products - yield on conversion for catalysts with various Pd-contents

+	Al <sub>2</sub> O <sub>3</sub>	carrier without Palladium	
Δ	"	"	with 0,02 % Pd
×	"	"	" 0,06 % "
•	"	"	" 0,1 % "
◦	"	"	" 0,5 % "
+	"	"	" 10 % "

The Al<sub>2</sub>O<sub>3</sub>-carrier, without Palladium, gives exclusively cracked products, e. g. at a conversion of 44 wt. % (reaction temperature 500°C) only 1,1 wt. % of normal hexane was to be found as branched hydrocarbons. Addition of small amounts of Pd to the Al<sub>2</sub>O<sub>3</sub>-carrier - 0,02 % - had no marked influence in decreasing the yield of cracked products.

The catalyst containing 0,06 wt. % Pd gives, at similar conversions, considerably smaller amounts of cracked products than the earlier catalysts.

An increase of the Pd-concentration to 0,1 wt. % caused, at similar conversions, an increased yield of C-6 isomers. By a further increase of the Pd-concentration to 0,5 wt. % the proportion between cracked and isomer products was shifted in favour of the cracked products.

The increase of the yield of cracked products becomes clearer with the catalyst containing 10 wt. % Palladium.

From the course of the curves in Fig. 1 and Fig. 2 it can be said that Palladium contents varying between 0,1 and 0,5 wt. % can be considered to be favourable for the isomerization. At lower and higher Palladium-contents the portion of the cracked products, at similar conversions, were increased.

## **2. Isomerisation and Hydrocracking of a soft paraffin wax with a 0,1% Pd on alumina-boria catalyst**

### **2.1 Reactor used**

The experimental runs, described in this report, were conducted with a half-continuous apparatus which differed slightly from the one used for the isomerization of a n-C<sub>12</sub> fraction (s. Final Technical Report, Nov. 30, 1961, 4.1. p. 20).

The reactor tube (23,5 mm i. d. ) of the new apparatus was 1100 mm long. It was surrounded by an aluminium block with electric heating coils. The temperature of the jacket was maintained constant at the desired values by a governing thermo couple. The temperature-profile of the catalyst bed could be measured with a movable thermo couple in a central thermo couple sheath tube (7 mm o. d. )

80 ml of catalyst were placed in the lower third of the reactor tube which had a constant temperature over the entire length. Quartz chips served as the lower catalyst support and Quartz chips were placed on top of the catalyst bed, too.

The liquid paraffin wax as well as hydrogen from a cylinder through a reducing valve were introduced at the top of the reactor tube.

The reaction products under pressure passed through a water-cooler and a gas-liquid separator from which the liquid products were drawn out through a needle valve. The gas from the gas-liquid separator, made up of hydrogen and reaction products, were passed over a condenser cooled by dry-ice and the uncondensed gas was measured by a gas meter.

### **2.2 Reaction conditions**

The experiments were conducted at a constant pressure of 50 atm and at a constant liquid hourly space velocity of 0,75 V/V/h, with different mole ratios of hydrogen to feed and at different temperatures.

a) mole ratio  $H_2$ : feed = 4,5 <sup>+)</sup>   
temperatures: 150°C and 375°C

b) mole ratio  $H_2$ : feed = 27 <sup>++)</sup>   
temperatures: 150°C, 375°C and 400°C

### 2.3 Feed composition

As feed a soft paraffin wax <sup>++)</sup> was used, with a cloud point of 33°C.

By the gas chromatographic analysis it was confirmed that the greater portion of the paraffin wax was composed of  $C_{19}$ - $C_{22}$  normal hydrocarbons.

Normal hydrocarbons with a C-number less than 19 formed approximately 10 % by weight of the wax. The lowest normal hydrocarbon was  $n-C_{15}H_{32}$ .

### 2.4 Catalyst

The catalyst used was: 0,1 % Palladium on an acid alumina borica carrier (grain size 1,5 - 3 mm). This catalyst was chosen as it was established to be suitable for the isomerization  $n-C_{12}$  to  $n-C_{14}$  fraction (s. Report Nov. 30, 1961, p. 2').

### 2.5 Results and discussion

For each run 250 cm<sup>3</sup> of liquid paraffin wax was used. Practically the same volume of reaction products was obtained in all cases.

In order to judge the extent of the isomerization, the liquid reaction products were fractionated into several fractions with a spinning band distillation column. The results are given in Table 1.

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<sup>+)</sup>  These values are valid for an average feed molecular weight of 215

<sup>++)</sup> supplied by the firm Schering AG, Werk Bergkamen

**Table 1** Isomerization of a soft paraffin wax at 50 atm  
over a Palladium catalyst  
(Yield in wt. % of liquid reaction product)

Fraction	mole ratio $H_2$ : feed = 4, 5		mole ratio $H_2$ : feed = 27		
	Reaction temperature		Reaction temperature		
	350°C	375°C	350°C	375°C	400°C
I. up to 100°C	0,69	3,85	0,66	5,04	7,71
II. 100 - 150°C	1,40	2,51	1,55	4,40	4,64
III. 150 - 255°C (Vacuumdistill.)	3,34	8,98	2,60	9,98	9,77
	5,43	15,34	4,81	19,42	22,12

IV. over 255°C

The collected fractions were separately analysed by gas chromatography with different selected columns in a Perkin-Elmer fractometer.

Fraction I : GA Perkin-Elmer column (length 10,40 m; i. d. 5 mm  
column temp. 50°C  
carrier gas :  $H_2$  1 atd)

Fraction II: GA Perkin-Elmer column (length 10,40 m; i. d. 5 mm  
column temp. 80°C  
carrier gas :  $H_2$  2 atd)

Fraction III: Apiezonfat on Sterchamol column  
(length 3,70 m; i. d. 4 mm  
column temp. 180°C  
carrier gas :  $H_2$  3 l/h)

The gas chromatography analysis of the fraction IV with a very short column (length 55 cm, apiezonfat on Sterchamol, column temp. 180°C) gave no satisfactory chromatograms (superpositions of the isomers and normal hydrocarbons). For this fraction which should have approximately the same initial boiling point as the feed, the cloud point was determined. The results of these analysis are given in table 2.

Table 2.

Isomerization of a soft paraffin wax at 50 atm  
over a Palladium catalyst  
(Yield in wt. % of liquid reaction product)

Hydrocarbons	mole ratio H <sub>2</sub> :feed = 4,5				mole ratio H <sub>2</sub> :feed = 27				
	Reaction temperature				Reaction temperature				
	350°C		375°C		350°C	375°C	400°C		
Propane		-		-			0.02		-
i-Butane	0.01		0.02		0.05		0.12	0.05	
n-Butane		0.04		0.05		0.06		0.18	0.13
i-Pentane	0.05		0.30		0.06		0.57	0.48	
n-Pentane		0.06		0.35		0.07		0.49	0.64
i-Hexane	0.12		0.32		0.07		1.11	1.77	
n-Hexane		0.07		0.68		0.09		0.72	1.35
i-Heptane	0.13		1.01		0.09		1.13	2.14	
n-Heptane		0.21		0.54		0.19		0.70	1.17
i-Octane	0.22		0.80		0.36		1.63	2.00	
n-Octane		0.32		0.45		0.27		0.74	0.76
i-Nonane	0.43		0.77		0.54		1.31	1.22	
n-Nonane		0.43		0.49		0.38		0.72	0.66
i-Decane	0.31		1.01		0.47		1.52	1.43	
n-Decane		0.33		1.05		0.34		0.89	0.84
i-Undecane	0.41		1.12		0.48		1.36	1.13	
n-Undecane		0.45		1.20		0.32		0.90	0.80
i-Dodecane	0.38		0.97		0.31		1.13	0.99	
n-Dodecane		0.40		0.94		0.24		0.83	1.05
i-Tridecane	0.32		0.83		0.12		1.13	0.37	
n-Tridecane		0.32		0.80		0.20		0.77	0.33
i-Tetradecane	0.17		0.40		0.00%		0.84	0.74	
n-Tetradecane		0.25		0.66		0.15		0.55	0.51
Σ	2.55		8.15		2.52		11.85	12.93	
Σ		2.38		7.19		2.31		7.57	9.14
Wax (m.p. up to 25.5°C) in	5.43		15.34		4.81		13.42	22.12	
Σ		46.9		58.1		52.2		61.0	58.7
Σ i-C <sub>n</sub> / Σ i-C <sub>n</sub> × 100									
Wax point (°C) of fraction over 25°C	30		27.5		28		26		23

From table 1 it can be seen that at a reaction temperature of 350°C approximately 5 % by weight of the paraffin wax were cracked to hydrocarbons boiling below 255°C. The yield of this fraction increased considerably at higher reaction temperatures. Thus at reaction temperatures of 375°C and 400°C this fraction amounted to 15 - 20 % and 22 % by weight respectively.

Table 2 shows that the yield of C<sub>4</sub>- and C<sub>5</sub>-hydrocarbons in the fraction < 255°C b. p. was small (max 6 wt %). The greater portion of this fraction was composed of C<sub>6</sub> - C<sub>13</sub> hydrocarbons. The percentage of the branched hydrocarbons depends on the reaction temperature and the mole ratio of hydrogen to feed.

Under equilibrium conditions, the branched chain C<sub>5</sub> hydrocarbons in the pentane fraction is 74 % wt. (at 375 °C) and the branched chain C<sub>6</sub> hydrocarbons in the hexane fraction is 80 % wt. (at 350 °C). In our experiments the branched chain hydrocarbons were 54 % wt. in the pentane fraction and 63 % wt. in the hexane fraction.

The difference in cloud points between the feed and the fraction boiling over 255°C was taken as a measure of the extent of isomerization and hydrocracking. This lowering of cloud point at a mole ratio of H<sub>2</sub> to feed of 27, 0 was greater than that at a mole ratio of H<sub>2</sub> to feed of 4, 5

	7°C	against	5.5°C	at a reaction temperature of	350°C
and	5°C	"	3.0°C	" " " "	" " 375°C

The maximum lowering of the cloud point (10°C) was obtained at a temperature of 400°C and at a mole ratio H<sub>2</sub> to feed of 27.

**3. Contribution to basic research on the analytic of isomers  
in the range C-6 up to C-9**

**Introduction**

By the isomerization of normal aliphatic hydrocarbons  $C_{12}$  and higher, the isomers obtained were comprehensively classified in the most cases as "branched isomers" without taking into consideration the individual isomers. This was done, as in this range it was very difficult to identify individual hydrocarbons, because of the large number of possible isomers. The modern analytical methods can give satisfactory solutions in cases of mixtures of hydrocarbons up to carbon atom seven. Above C-7 is the number of the possible isomers large enough to make such an analytical problem solvable only under favourable conditions<sup>1, 2)</sup>.

The method, which has been applied with success for the analysis of hydrocarbons is gas chromatography and particularly for the determination of individual components a combination of gas chromatography with mass-spectrometry<sup>3)</sup>.

For the separation of saturated branched isomers by gas chromatography, use is made principally of the difference in their boiling points rather than of the difference in the special arrangement of the molecules. The difficulty due to the small difference in volatility can be partially overcome by using a column with a large number of theoretical plates, wherein compounds are separated according to the order of their boiling points. For close boiling isomers which are not separated in the above column, a second column with special selectivity for the different isomers can be used.

By a combination of such columns, wherein the fraction from the first column is run into the second column, the possibility of resolving a mixture is increased. Pure compounds, obtained as fractions from the second column, can then be easily identified by means of mass spectrometry.



### 3.1 Gas chromatography of normal and branched isomers

Before attempting an analysis of branched hydrocarbons in a mixture, the preliminary determination of retention volume data of a number of pure hydrocarbons is beneficial, so far as such data are not available.

#### 3.1.1 Relative retention volumes of pure compounds

Materials employed: The hydrocarbons employed in this investigation belong to a remarkable collection of pure compounds of our Institute. A great number of these were supplied by the National Bureau of Standards, Washington. A complete list of the physical properties is not given here, as only the boiling points are significant in the determination and correlation of retention volume data.

As stationary phase liquids silicone oil AR 500 furnished from Wacker-Chemie (Munich) and 7.8 benzoquinoline were used.

Sterchamol (particle size 0,3 - 0,4 mm) was used as the inner support for both the stationary phase liquids.

Experimental: The columns consisted of 6 mm Ermeto tubing contained in a thermostatically controlled, electrically heated oven with circulating air bath. Detection was by thermal conductivity. The recording potentiometers were operated at 1 mV to 10 mV for full scale deflection. The operating conditions for both columns are listed in Table 3.

Table 3 Operating conditions

	7.8 benzoquinoline column	silicone oil column
amount of liquid phase/ amount of stat. phase, w/w.	30/100	40/100
length, meter	20	25
carrier gas	hydrogen	hydrogen
operating temperature, °C	80	100
flow rate of H <sub>2</sub> , l/h	2,4	2,7
sample size, microliters	10	10

The relative retention volumes of 37 hydrocarbons have been determined on both columns using n-nonane as the reference substance throughout. The results are given in Table 4.

The operating time for the emergence of the higher boiling component (n-nonane) was in the case of 7.8 benzoquinoline column apprx. 4, 5 hours and in the case of silicone oil column apprx. 6 hours..

The efficiencies of both columns have been calculated. The number of theoretical plates was for the 7, 8 benzoquinoline column about 7000 and for the silicone oil column about 9000.

Table 4 Relative retention volumes of saturated hydrocarbons

a) aliphatic hydrocarbons <sup>1)</sup>

	measured rel. ret. volume on silicone oil column	measured rel. ret. volume on 1.8 benzoquinoline column	Boiling Point °C
n-nonane	1.0000	1.0000	150.8
2-m	0.778	0.687	143.3
3-m	0.826	0.738	144.2
3,3,4-trim	0.735	0.687	140.5
2,3,3-trim	0.691	0.582	137.7
2,2,3-trim	0.611	0.468	133.6
2,3,5-trim	0.567	0.421	131.3
2,4,4-trim	0.546	0.421	130.6
2,2,4-trim	0.482	0.330	126.5
2,2,5-trim	0.439	0.269	124.1
2,3,3,4-tetram	0.805	0.714	141.6
2,2,3,3-tetram	0.776	0.650	140.3
2,2,3,4-tetram	0.611	0.468	133.0
2,2,4,4-tetram	0.419	0.282	122.9
n-octane	0.500	0.445	125.6
3-m	0.419	0.330	119
2,5-dim		0.210	109
2,3,3-trim	0.394	0.296	114.2
2,2,3-trim		0.236	110.3
2,2,4-trim	0.222	0.144	99.3
n-heptane	0.249	0.191	98.4
2-m	0.196	0.133	89.7
3-m		0.148	91.8
3,3-dim		0.117	86.0
2,4-dim		0.089	80.8
2,2-dim		0.086	79.9
2,2,3-trim	0.167	0.094	80.8

b) alicyclic and aromatic hydrocarbons

cycloheptane	0.582	0.562	119
cyclohexane	0.222	0.173	80.7
methylcyclohexane	0.334	0.282	100.3
ethylcyclohexane	0.718		131.8
dimethyl, 1,2-cyclohexane	0.518		130.3
diethyl, 1,2-trans-	0.567		123.4
diethyl, 1,4-trans-	0.432		119.0
dimethyl, 1,3-cis-	0.682		119.5
cyclopentane		0.083	49.3
benzene	0.251	0.421	80.1

<sup>1)</sup> please note that for the designation of the aliphatic hydrocarbons in each series the base hydrocarbon name is lower by one for singly methylated, two for 2 methyl branches etc., e. g. n-nonane 2-methyloctane etc.

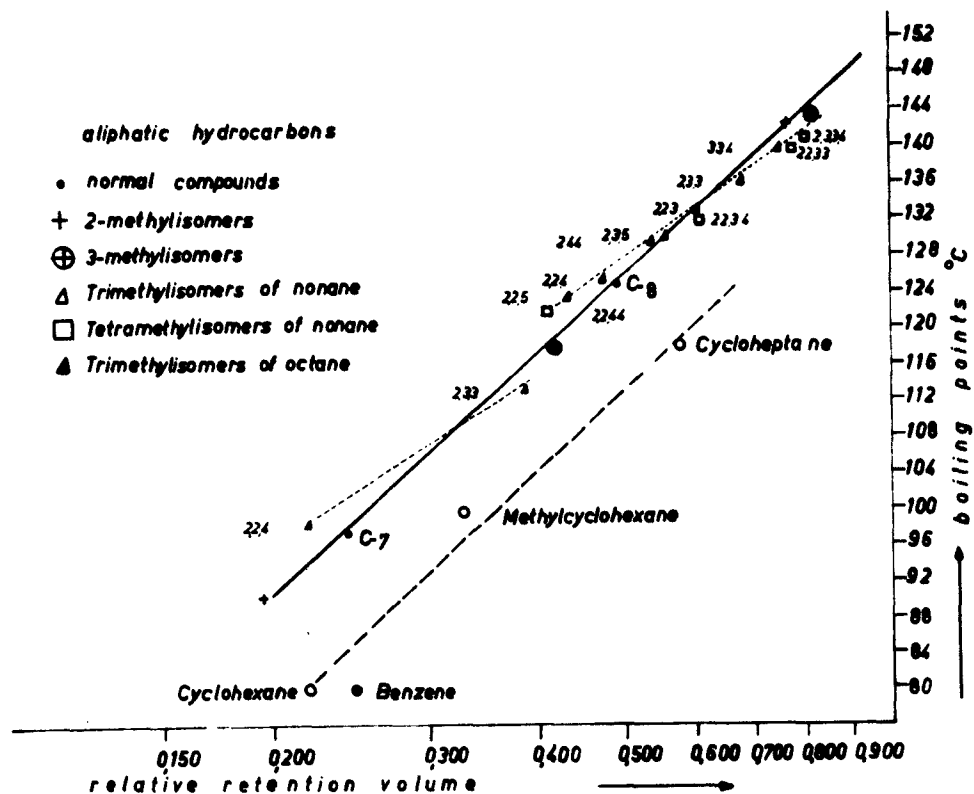


Fig. 3 Selectivity of Silicone oil at 100°C

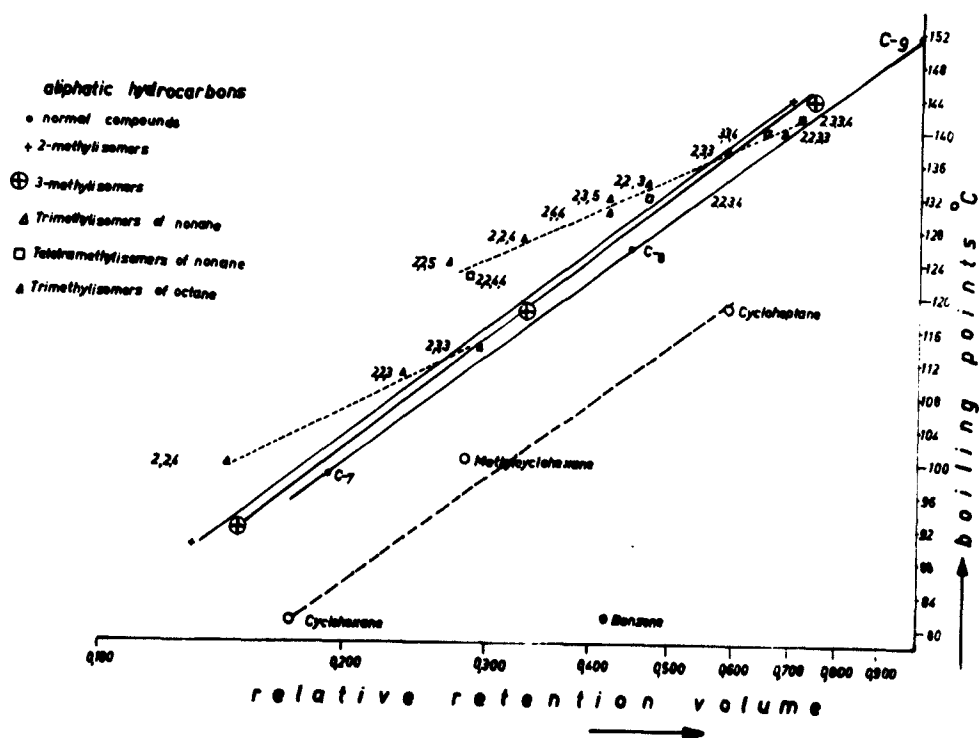


Fig. 4 Selectivity of 7.8 benzquinoline at 80°C



Fig. 5 Chromatogram of the synthetic blend (Column: silicone oil, length 25 m, operating temp 100°C, carrier gas hydrogen, flow rate 2, 7 l/h)

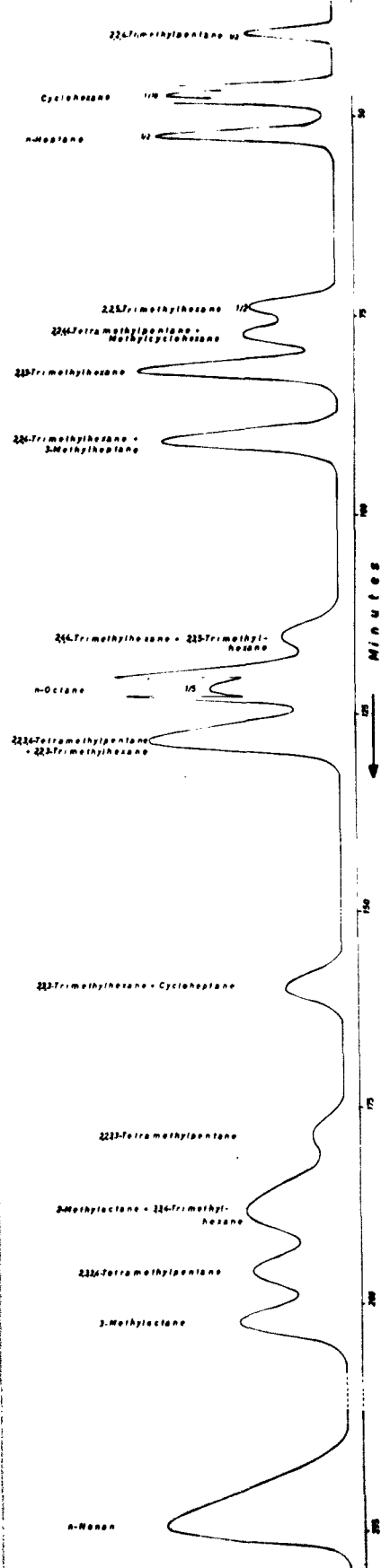
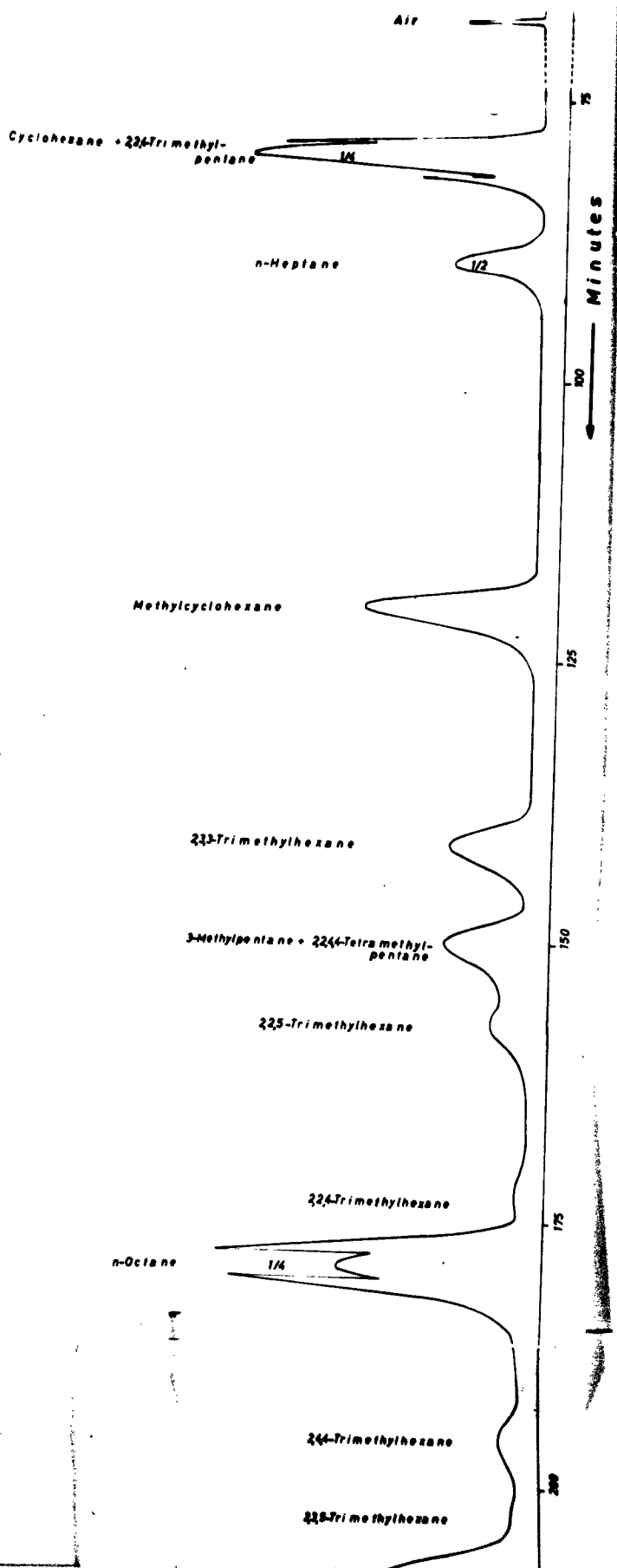
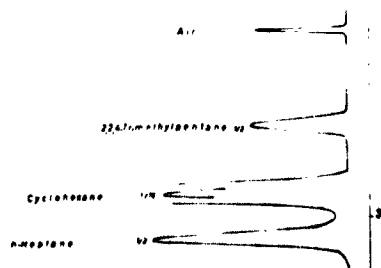


Fig. 6 Chromatogram of the synthetic blend (Column: 7, 8 benzoquinoline, length 20 m, oper. temp. 80°C carrier gas hydrogen, flow rate 2.4 l/h)



7 1/h)



2, 4 1/h)

### 3.1.2 Discussion

The relative retention volumes given in table 4 have been plotted in figures 3 und 4 against the boiling points.

With the silicone oil column, which is relatively unselective, the separation is substantially dependent on volatility. However, among the hydrocarbons of different molecular types a small separation takes place, e g. between naphthenes and paraffins the separation takes place to an extent of about 12°C and between aromatics and paraffins to an extent of about 20°C.

Normal paraffins, 2-methyl and 3-methylisomers lie practically on the same line.

A slight irregularity has been observed with the trimethyl- and tetramethyl-isomers of nonane and also with trimethyl isomers of octane. They lie on lines intersecting the earlier one.

With the 7.8 benzoquinoline column, which is a highly polar phase, the separation between the different molecular types is more pronounced, the naphthenes being separated from paraffins by an amount equivalent to about 15°C and the aromatics from the paraffins to an extent of nearly 40°C.

Each homologous series of the paraffins produces a straight line. The n-paraffin, 2-methyl- and 3-methylisomer lines are approximately parallel to each other. Trimethyl- and tetramethyl isomers of nonane as well as trimethylisomers of octane lie on lines intersecting the earlier ones. The deviation of the last lines from the parallelism is here much more pronounced than in the case of the silicone oil column.

Branched hydrocarbons which cause to a great extent this irregularity are the 2.2.4.4 tetramethylpentane  
2.2.5- and 2.2.4 trimethylhexanes  
and 2.3.4 trimethylpentane

that is hydrocarbons whose CH<sub>3</sub>-groups are distributed particularly to both ends of the molecule.

The chromatograms of a 22-component synthetic mixture of mostly branched isomers of nonane on 7. 8 benzoquinoline column and silicone oil column are given in Fig. 5 and Fig. 6.

The separation possibilities with the above columns either alone or in combination have been considered on the basis of the above mixture.

Each of the above columns separates very well the following seven hydrocarbons: n-nonane, 3 methyloctane (b. p. 144, 2°C), 2. 3. 3. 4 tetramethylpentane (b. p. 141, 6°C), n-octane (b. p. 125, 6°C), 2. 2. 5 trimethylhexane (b. p. 124, 1°C), 2. 3. 3 trimethylpentane and n-heptane.

With the 7, 8 benzoquinoline column it has been possible to separate in addition to these seven hydrocarbons the following also:

2. 2. 3. 3 tetramethylpentane (b. p. 140, 3°C) from 2, methyloctane (b. p. 143, 3°C) and cyclohexane (b. p. 80, 7°C) from 2. 2. 4 trimethylpentane (b. p. 99, 3°C). In spite of the fact, that the differences in boiling points of the components in each pair were large enough (3°C and 18, 6°C), they could not be separated with the silicone oil column as the separation due to the difference in type and molecular structure compensated exactly the separation due to the difference in volatility.

With the silicone oil column, it has been possible to separate in addition to the above mentioned sever hydrocarbons the following also:

2. 4. 4 trimethylhexane (b. p. 130, 6°C) from 2. 3. 5 trimethylhexane (b. p. 131, 3°C)  
2. 2. 4. 4 tetramethylpentane (b. p. 122, 3°C) from methylcyclohexane (b. p. 100, 3°C)  
2. 2. 4 trimethylhexane (b. p. 126, 5°C) from 3-methylheptane (b. p. 119°C)  
2. 2. 3 trimethylhexane (b. p. 137, 7°C) from cycloheptane (b. p. 119°C)  
2-methyloctane (b. p. 143, 3°C) from 3. 3. 4 trimethylhexane (b. p. 140, 5°C)  
All these pairs could not be separated with the 7. 8 benzoquinoline column.

Summarizing, it has been possible to determine from the 22-component synthetic mixture

by means of the 7. 8 benzoquinoline column 10 components  
by means of the silicone oil column 14 components  
and by the combination of both the columns 20 components.



### **3.2 Investigation on the composition of a isomerizate by a combination of gas chromatography and mass - spectrometry**

In the analysis of an unknown mixture of hydrocarbons by the gas-chromatography the use of a single column gives usually unsatisfactory results, as some of the peaks consist of more than one component. The resolution of these fractions can be often achieved by collecting them individually and rerunning them on another column with a different selectivity. Pure compounds can then be identified easily by means of mass-spectrometry.

A similar technique has been made use of by us in this work, with a mixture of branched isomers as sample.

#### **3.2.1 Occurence of the sample**

The investigated sample was a product obtained by the isomerization of normal nonane with Palladium on boria-alumina as catalyst. The experimental run has been conducted with a continuous apparatus under the following operating conditions: reaction temperature 400°C; pressure 50 atm; liquid hourly space velocity 0,5 Vol. /Vol. /h; mol  $H_2$  / HC 4. This product is named thereupon "isomerizate".

#### **3.2.2 Experimental procedure**

The collection of a fraction at the end of one column for the purpose of rerunning it on another column has been conducted by means of a special U-tube trap. The U-tube, filled with sorption material (chromosorb, particle size 0,3 - 0,4 mm) was provided with a four-way stopcock allowing the gas flow to be diverted at will through it or by-passed across it (Fig. 7). The whole system was connected to the outlet of the column by means of a heat-resistant silicone-tube. Gas lines from detector to the trap were heated by electrical resistance wire to a temperature slightly above the operating temperature of the column to avoid condensation of

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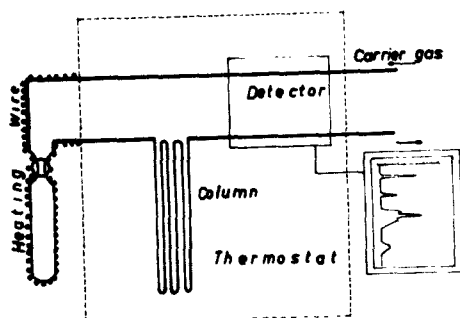


Fig. 9 Arrangement for introducing enriched samples in the chromatograph

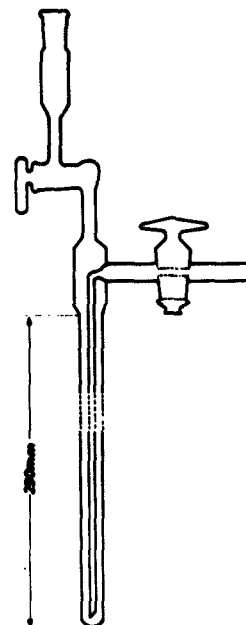


Fig. 10 Fraction collector

For investigations by means of mass spectrometry the collection of a fraction was carried out with a trap immersed in a liquid air bath. The trap was sufficiently long (29 cm) to ensure complete condensation (Fig. 10).

Mass spectras have been obtained with a spectrometer Atlas-CH<sub>3</sub>-apparatus.

### 3.2.3 Correlation of compounds in the chromatogram

#### Identification by means of gas chromatography

With a single column an identification of the components of the isomerizate has been attempted. A chromatogram of this isomerizate on a 7.8 benzoquinoline column is given in Fig. 11.

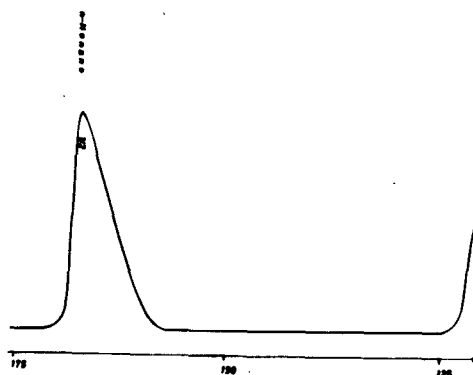


Fig. 11 Chromatogram of the isomerizate  
(column: 7, 8 benzoquinoline, length 15 m, operation temp. 80°C,  
carrier gas hydrogen, flow rate 3 l/h)

The last peak appearing represents the unreacted normal nonane. The peaks appearing before n-hexane could also be easily identified. These are in the order of their emergence: propane, isobutane, n-butane, isopentane, n-pentane, 2,2 dimethylbutane, 2,3 dimethylbutane, 2-methylpentane, 3-methylpentane.

From the peaks appearing between n-nonane and n-hexane a prediction about the nature of components could be made only for peaks "a" and "b". These peaks, according to their retention volumes represent isomers of nonane with high boiling points. Such isomers of nonane are relatively small in number, as can be seen from Fig. 12.

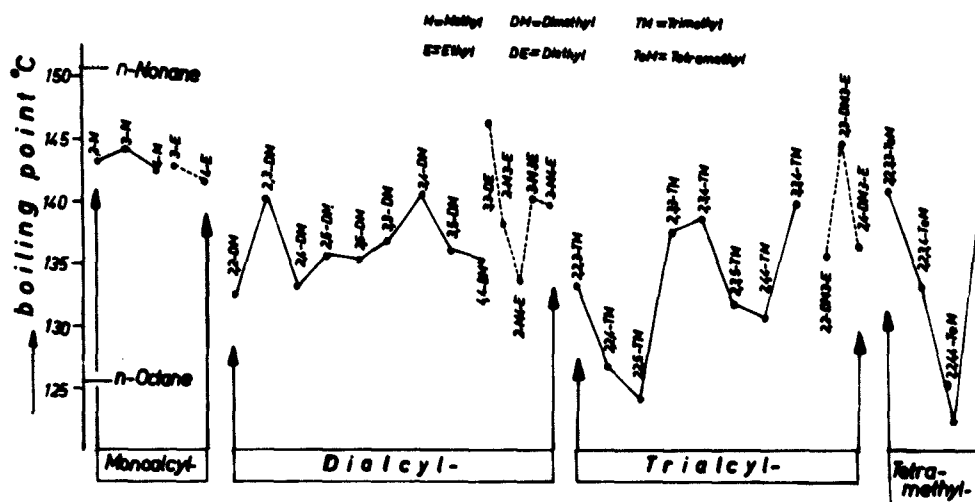


Fig. 12 Boiling points of the C-9 isomers

Thus by the comparison of the relative retention volumes of peaks "a" and "b" with those of known compounds and from a consideration of the kinetic aspects of the isomerization it could be confirmed that the peak "a" contained 3-methyl-octane and the peak "b" 2-methyloctane.

For the other peaks (c, d, e, . . . .) it has not been possible to identify compounds in spite of the fact that some of these peaks showed similar retention data to that of known isomers of nonane because other isomers whose retention data were not available could as peaks c, d, e . . . . come out on account of their boiling points in the same position in the chromatogram.

From the chromatogram of the isomerizate on a silicone oil column the assumed identification for some of the hydrocarbons could be confirmed further. As shown in Fig. 3 and 4 some isomers of C-9 are retarded

relatively stronger in the silicone oil column than in the 7.8 benzoquinoline column. This property is later made use for the characterization of hydrocarbons for which only the C-number could be predicted from the mass spectra.

In order to find whether the substance appearing under one peak consisted of one or more components, the substance appearing under a peak from the 7.8 benzoquinoline column has been collected and rerun into the silicone oil column. Under favourable conditions the mixture could be separated into its constituents. Thus the peaks "a" and "e" could be resolved into the peaks "a<sub>1</sub>" and "a<sub>2</sub>" and "e<sub>1</sub>" and "e<sub>2</sub>" respectively, whereas peaks b, c, d . . . . remained unresolved. This result, however, was useful for the identification by mass spectrometric investigations.

#### Identification by means of mass spectrometry

A particularly suitable method for the identification of peaks on the chromatogram is the direct investigation of collected compounds by means of the mass spectrometry. The determination of the molecular weight of a compound, which generally can be known from the mass spectra, gives a very precious first indication for the nature of the compound, e. g. to predict to which molecular type (paraffin or naphthen or aromatic) the substance belongs.

From the distribution of the masses on a spectre one can often further characterise the compound under consideration. This characterisation is facilitated in many cases from the broad collection of mass spectra by the "American Petroleum Institute" (API).

The extent to which a precise identification of the compound under consideration can be achieved depends on many factors. For example, it is of importance to know if the fraction under investigation contains one or more components. In the case where more components are

present, the identification becomes difficult depending on the ratio in which the components are present. Finally it is important to consider whether one relies for identification on the mass spectra using the same mass spectrometer obtained from known compounds or in the API catalogue since the mass spectra obtained from different mass spectrometers differ from one another.

As it is possible to make a qualitative analysis using a mass spectrometer, the same has been made use of to analyse the isomerizate. Fractions represented by the peaks a, b, c, d, . . . on the chromatogram (Fig. 11) were collected by liquid air cooling as described in p. 21 and after heating to room temperature were introduced into the mass spectrometer. From the obtained spectra an attempt has been made to identify the components. The results of the correlation for a number of peaks are given in Table 5.

**Table 5** Results of the characterization by means of mass spectrometry for the peaks of chromatogram Fig. 11

Peak	characterized compounds
a $\begin{cases} a_1 \\ a_2 \end{cases}$	3-methyloctane 3, 4 dimethylheptane <sup>+</sup> )
b	2-methyloctane + 4 methyloctane
c	2, 3 dimethylheptane + C <sub>9</sub> H <sub>18</sub>
d	2 methyl 3 ethylhexane
e $\begin{cases} e_1 \\ e_2 \end{cases}$	C-9 paraffin(s) C-9 paraffin(s)
f	2, 5 dimethylheptane + C <sub>9</sub> H <sub>18</sub>
g	C-9 paraffin(s)
h	C-8 paraffin
k	C-9 paraffin(s) (eventually 2, 2 dimethylheptane)
l	C-8 paraffin + C <sub>7</sub> H <sub>14</sub>
m	C-8 and C-9 paraffins
n	C <sub>7</sub> H <sub>14</sub>
o	C-9 paraffin(s) + event. C <sub>7</sub> H <sub>14</sub>
r	C-7 paraffin + C <sub>6</sub> H <sub>12</sub>

<sup>+</sup>) Identification not certain

From table 5 it is seen that the earlier peaks a, b, c, d could be identified with certainty. For the majority of the remaining peaks, only the molecular weight could be determined, as the peaks were composed of more than one isomer, whose mass spectra are not very much different from one another.

The procedure of the identification of a fraction is in more detail discussed taking peak "d" as an example. The mass spectra of this fraction obtained with our Atlas-CH<sub>3</sub>-apparatus showed a distribution as in Table 6.

Table 6      Relative intensities of mass spectra

Mass Charge Ratio	Relative Intensities	
	Peak "d"	2-methyl 3 ethylhexane
41	29.0	30
42	9.5	10.4
43	100	100
55	14.6	13
56	17.7	12
57	58.6	35
69	10.6	7.0
70	6.4	1.6
71	12.7	4.1
84	36.2	32
85	31.9	27
98	2.7	1.1
99	4.6	2.4
113	0.8	0.1
126	1.6	0.7

From the mass spectra it was seen that the substance under consideration was C-9 paraffin. A comparison with the mass spectra from the API-catalogue of all the 35 C-9 paraffins led to the conclusion that the peak "d" consisted of 2 methyl 3 ethylhexane.

By some mass charge ratios the difference in the relative intensities for the component from peak "d" and for 2-methyl 3 ethylhexane from



the API catalogue is comparatively large. However, it is to be noted that when mass spectras from different mass spectrometers are compared a difference of the above order is usually to be noticed. The intensity by higher masses, for paraffins from the Atlas- $\text{CH}_3$ -apparatus is mostly larger than by the CEC-apparatus. However, the ratio of the intensities between the neighbouring masses is nearly the same. Therefore, in spite of the differences, with a certain amount of precaution identifications can be made as given in Table 5 by the method shown in Table 6.

In Table 7 are summarized the results of the characterization of the peaks on the chromatogram Fig. 11 by means of both methods: mass spectrometry and gas chromatography.

As shown, with the help of the retention data of a peak the possible number of substances predicted on the basis of the mass spectre could sometimes be limited. In some cases the determination of the molecular weight in addition to the retention volume data could give more definite indications for an isomer.

**Table 7** Summary of the results of the characterization of the peaks on the chromatogram Fig. 11 by a combination of mass spectrometry and gas chromatography

Peak	characterized compounds
a { $a_1$ $a_2$	3-methyloctane 3, 4 dimethylheptane <sup>+) </sup>
b	2-methyloctane + 4-methyloctane
c	2, 3 dimethylheptane + C-9 olefin
d	2-methyl 3-ethylhexane
e { $e_1$ $e_2$	C-9 paraffin(s) C-9 paraffin(s)
f	2, 5 dimethylheptane + C-9 olefin
g	C-9 paraffin(s)
h	normal octane
k	C-9 paraffin(s) (eventually 2, 2 dimethylheptane)
l	C-8 paraffin + $\text{C}_7\text{H}_{14}$
m	C-8 and C-9 paraffins (evtl. 2, 2, 4, 4 tetramethyl- pentane)
n	$\text{C}_7\text{H}_{14}$
o	C-9 paraffin(s) (evtl. 2, 2, 5 trimethylhexane) + event. $\text{C}_7\text{H}_{14}$
r	$\text{C}_8\text{H}_{18}$ + $\text{C}_7$ paraffin (evtl. 3, 3 dimethylpentane)

<sup>+)</sup>  Identification not certain

### 3.2.4 Quantitative analysis

For a quantitative analysis of the isomerizate the areas of the peaks from the chromatogram Fig. 11 were measured assuming that the area is proportional to the weight of the compounds represented by them. Areas for partially separated peaks or shoulders were defined by dropping a perpendicular from the minimum or inflection point to the base line.

For multi-component peaks for which a resolution by means of a second column has been achieved, relative peak areas of individual constituents were determined. For those not resolved in the above manner, it has been often possible on the basis of the mass spectre to predict the kind of the compounds consisting them. For a number of peaks only the determination of the molecular weight was possible.

Taking into consideration the above aspects a quantitative estimation of the following components of the isomerizate could be given (Table 8).

Table 8 Composition of the isomerizate

Hydrocarbons	wt. % of liquid reaction product
propane	0.28
isobutane	1.29
n-butane	1.92
iso-pentane	3.48
n-pentane	2.84
2.2 dimethylbutane	0.14
2.3 dimethylbutane	0.11
2-methylpentane	0.97
3-methylpentane	0.65
n-hexane	1.55
C <sub>6</sub> (olefins+naphthenes) + C <sub>7</sub> (olefins + naphthenes + paraffins) - C <sub>8</sub> paraffins	0.4
3-methyloctane	12.6

3-4 dimethylheptane ++)	0.3
2-methyloctane + 4 methyloctane	20.4
2.3 dimethylheptane +)	1.0
2 methyl 3 ethylhexane	0.17
2.5 dimethylheptane +)	2.8
C-9 isoparaffins (not monoalkylisomers)	5.7
C-9 isoparaffins (not mono- or dialkylisomers)	0.1
normal nonane	43.1
fraction boiling over 152°C	0.2

+ ) contaminated with C-9 olefins at a concentration  
of appr. 20 : 1

++ ) Identification not certain

#### 4. Catalytic isomerization of n-nonane with a Palladium on Alumina-Boria as catalyst

The experimental runs were conducted using both continuous and batch operations. As feed normal nonane <sup>+)</sup>  was used in both cases.

##### 4.1 Continuous operations

###### Reactor used

The apparatus for the experimental runs was the same as the one used for the Isomerization and hydrocracking of a soft paraffin wax (s. p. 6).

The volume of the catalyst was 70 ml. It was placed in the lower third of the reactor tube having a constant temperature. The filtered normal nonane and hydrogen from a cylinder through a reducing valve were introduced at the top of the reactor tube.

The reaction products under pressure passed through a water cooler and came to a separator. The gas from the separator, made up of hydrogen and reaction products, was passed through a trap immersed in dry-ice methanol mixture. Gases condensed in this trap were mixed with the liquid separated in the separator and served as sample for analyses.

##### 4.1.2 Reaction conditions

The experiments were conducted at a constant pressure of 50 atm and at a constant mole ratio of hydrogen to feed of 4 with different space velocities and temperatures.

The reaction conditions were the following:

a) space velocity = 0,5 V/V/h  
temperatures: 375°C, 400°C, 425°C

b) space velocity = 2 V/V/h  
temperatures: 375°C, 400°C, 450°C

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<sup>+)</sup>  supplied by the firm Fluka AG - Chemische Fabrik Buchs SG -  
Switzerland

#### **4.1.3 Catalyst used**

The catalyst used was: 0,27 wt. % Palladium on an acid alumina-boria carrier (grain size 1-3 mm)

#### **4.1.4 Results and discussion**

For each run a volume of apprx.  $40 \text{ cm}^3$  normal nonane was used. The reaction products were chromatographed by means of a 7.8 benzoquinoline column. For a quantitative analysis, the areas of emerged peaks were measured; the nature of them was determined by comparison of their retention volumes with retention data obtained from a previous investigation of an isomerizate (see p. 27)

Results gives the Table 9

**Table 9** Isomerization of normal nonane over a Palladium catalyst  
(mole ratio  $H_2$ :HC = 4; pressure: 50 atm)

Yields in wt. % of liquid reaction product

Hydrocarbons	reaction temperature 375°C		reaction temperature 400°C		reaction temperature 425°C		react. temp. 450°C
	LHS:2 V/V/h	LHS:4, 5 V/V/h	LHS:2 V/V/h	LHS:0, 5 V/V/h	LHS:2 V/V/h	LHS:0, 5 V/V/h	LHS:2 V/V/h
propane	0.02	0.09	0.06	0.28	0.73	0.67	2.54
isobutane	0.06	0.63	0.19	1.29	1.88	2.76	6.99
n-butane	0.11	1.12	0.35	1.92	3.17	4.54	12.1
isopentane	0.18	2.44	0.49	3.48	4.41	7.78	14.8
n-pentane	0.18	2.40	0.44	2.84	3.36	5.99	13.4
2, 2-dimethylbutane	0.007	0.15	0.02	0.14	0.14	0.31	0.68
2, 3-dimethylbutane	0.007	0.11	0.025	0.11	0.15	0.23	0.68
2-methylpentane	0.10	0.88	0.24	0.97	1.30	2.07	4.78
3-methylpentane	0.07	0.64	0.17	0.65	0.98	1.47	8.48
n-hexane	1.03	1.45	1.73	1.55	3.43	2.39	5.03
$C_6$ (olef. + naph. + $C_7$ (olef. + naph. + paraf.) + $C_8$ paraf.	0.4	0.8	1.6	0.4	1.4	2.6	1.2
3-methyloctane + 3, 4 dimethylheptane	7.5	10.3	10.0	12.9	13.7	11.7	5.9
3-methyloctane + 4-methyloctane	11.4	16.5	15.5	20.4	21.8	19.1	10.1
2, 3-dimethylheptane +)	0.4	0.7	0.6	1.0	1.3	1.2	0.9
2-methyl 3-ethylhexane	0.03	0.19	0.09	0.17	0.35	0.29	0.04
2, 5-dimethylheptane +)	0.9	2.0	1.3	2.8	3.2	3.0	1.3
C-9 isoparaffins (not mono-alcylisomers)	1.7	4.3	2.8	5.7	6.7	6.6	4.4
C-9 isoparaffins (not mono- or dialcylisomers)	0.01	0.2	0.1	0.1	0.4	0.4	-
normal nonane	75.9	54.9	64.3	43.1	30.4	26.0	6.6
fractions boiling over 152°C	-	0.2	0.01	0.2	1.2	0.9	5.1

+ ) contaminated with C-9 olefins at low concentrations

+ + ) identification not certain

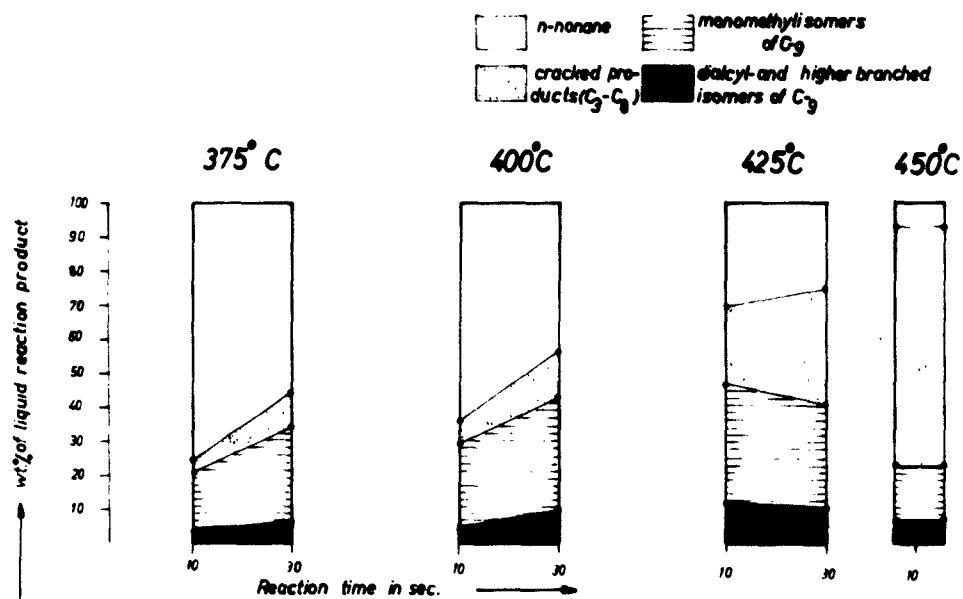


Fig. 13 Composition of the reaction products

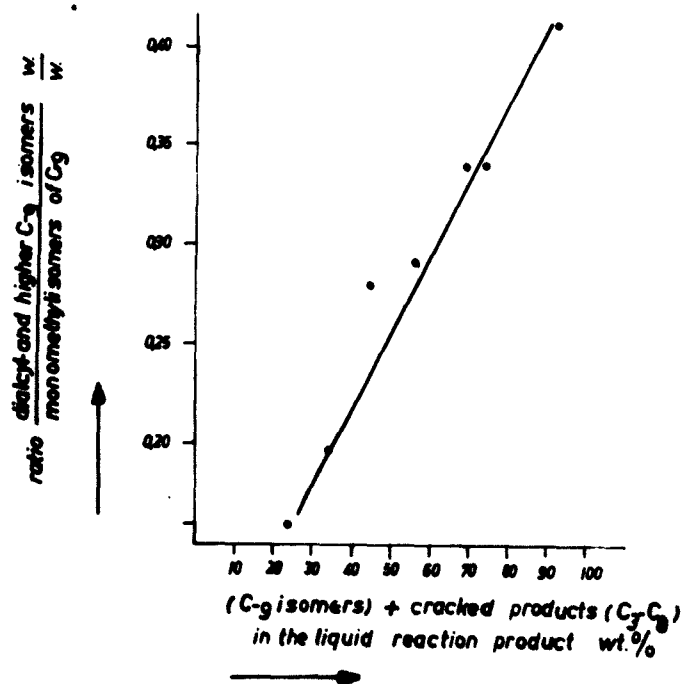


Figure 14

Yield of C-9 isomers and cracked products ( $C_3-C_8$ ) are plotted in Fig. 13 against the reaction time. Reaction times were calculated and found to be 10 sec. in the case of the experiments with space velocity 2 V/V/h and 30 sec. in the case of the experiments with space velocity 0,5 V/V/h.

At a temperature of 375°C was the isomerization of normal nonane considerably high. In general an increase in the reaction temperature from 375°C to 425°C increased the yield of C-9 branched hydrocarbons and above 425°C decreased in favours of cracked products.

The greatest yield of C-9 branched hydrocarbons was obtained at a reaction temperature of 425°C and at a reaction time of 10 sec (apprx. 47 wt. % of the liquid reaction product). Longer reaction times at a constant reaction temperature gave larger amounts of cracked products. In a similar way, longer reaction times affected the yield of C-9 branched isomers at reaction temperatures of 375°C and 400°C.

In the branched isomers of the C-9 fraction, the monomethyl ones represented the largest portion (over 70 wt. %).

The ratio  $\frac{\text{dialkyl- and higher C-9 isomers}}{\text{monomethylisomers of C-9}}$  plotted against the sum of C-9 isomers and cracked products ( $C_3-C_8$ ) formed is given in Fig. 14.

It is seen that this ratio is shifted in favour of the dialkyl- and higher branched isomers by an increase of the sum (C-9 isomers + cracked products.)

In the cracked products ( $C_3-C_8$ ) the amount of iso- $C_4$  in the C-4 fraction at reaction temperatures above 400°C corresponded to that of a thermodynamic equilibrium.

Under equilibrium conditions, and in the temperature range 375 - 425°C the branched chain  $C_5$  hydrocarbons in the pentane fraction are 74 - 70 wt. %, and the branched chain  $C_6$  hydrocarbons in the hexane



fraction are 80 - 77 wt. %. However, in this work values of 50 - 56 wt. % for the pentane fraction and 55 - 65 wt. % for the hexane fraction were obtained.

#### 4.2 Batch operations

##### Autoclave used

The autoclave was a small stainless steel bomb of 30 ml capacity, equipped with a manometer and a thermocouple in a central well connected to a temperature controller. Heating of the bomb was effected by an electrical oven of 500 watt in which the bomb fitted tightly. After the bomb had been filled, it was placed in the oven and the oven was mounted on a mechanical shaker. Reaction temperature was reached in about 20 minutes. Cooling of the autoclave to room temperature was accelerated by removing the bomb from the oven 15 minutes after the current had been switched off. Rapid cooling was important in order to suppress further reaction. After expanding and venting the gas which consisted of hydrogen and reaction product gases, the liquid product was collected for the analyses.

##### 4.2.2 Catalysts

The catalysts used were an alumina-boria carrier with Palladium contents ranging between 0,1 - 0,5 wt. %. Palladium in these concentrations gives as shown in page 5, large yields of branched hydrocarbons in the case of normal hexane as feed.

For the preparation of the alumina-boria carrier almost the same procedure was used as in p. 1. The only difference was that here the precipitation of aluminium nitrate and boric acid with ammonia was carried out at 0°C. Precipitation at this temperature gave carriers with larger surface area. The extent to which the precipitation-temperature affected the surface - area of the carriers is shown in Table 10.

**Table 10** Effect of the precipitation-temperature on the surface-area of an alumina boria carrier

precipitating temperature °C	surface of carrier (by Houl method) m <sup>2</sup> /g
0	459
10	382
20	218

For the impregnation of alumina-boria carrier with Palladium chlorid solution, particles of size 0,1 - 0,3 mm were selected. Preliminary runs with the autoclave have showed that optimal concentrations of Palladium for the isomerization of normal nonane is about 0,3 wt. %.

For the following investigations a catalyst of the composition  $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$  (4:1) + 0,27 wt. % Pd was used.

#### 4.2.3 Reaction conditions

The experiments have been conducted at different temperatures and reaction times

- a) reaction temperature: 375°C  
reaction time: 1 h, 4 h, 20 h
- b) reaction temperature: 400°C  
reaction time: 4 h
- c) reaction temperature: 425°C  
reaction time: 2 h, 4 h, 8 h

Each filling of the bomb consisted of 10 ml n-nonane, 3,2 g of catalyst and 50 atm of hydrogen. The mole ratio  $\text{H}_2$  to hydrocarbon was approx. 0,7

#### 4.2.4 Results and discussion

The reaction products were analysed by gas chromatography, with a 7,8 benzoquinoline column. Quantitative analyses of the emerged peaks have been carried out as in No. 4.1.4 of this report.

The results are given in the Table 11 (page 37).

Table 11 Isomerization of normal nonane with a Palladium catalyst (batch operations)

Yields in wt. % of liquid reaction products

Hydrocarbons	reaction temperature: 375°C (pressure: 160-165 atm)			react. temp.: 400°C (pres.: 160 atm)			reaction temperature: 425°C (pres.: 170 atm) (pres.: 175 atm) (pres.: 180 atm)		
	1 h	4 h	20 h	4 h	2 h	4 h	2 h	4 h	8 h
	react. time	react. time	react. time	react. time	react. time	react. time	react. time	react. time	react. time
propane	0.03	1.73	1.28	1.45	3.00	2.23	-	-	-
isobutane	0.18	0.72	2.46	1.06	0.29	0.40	0.16	0.60	0.60
n-butane	0.45	2.97	7.03	6.02	10.2	29.4	2.23	2.23	2.23
isopentane	1.51	2.86	7.92	4.08	1.55	1.61	13.5	13.5	13.5
n-pentane	1.23	4.74	8.65	9.94	17.4	11.6	0.04	0.04	0.25
2,2-dimethylbutane	0.06	0.12	0.27	-	-	0.18	0.89	0.89	0.89
2,3-dimethylbutane	0.07	0.13	0.29	-	-	0.99	3.30	3.30	3.30
2-methylpentane	0.73	1.57	3.23	2.40	0.58	0.75	1.21	1.21	1.21
3-methylpentane	0.49	1.29	2.19	1.55	0.48	0.32	23.1	23.1	23.1
n-hexane	0.91	6.45	4.01	11.2	14.0	9.32	-	-	-
C <sub>8</sub> (2-methyl + naphthyl + C <sub>7</sub> (olef. + naphthyl + paraf.)) + C <sub>8</sub> paraf.	2.7	8.5	5.2	10.0	8.3	6.3	22.2	22.2	22.2
3-methyloctane + 3,4-dimethylheptane	3.1	9.2	11.3	5.2	1.1	1.2	2.0	2.0	2.0
2-methyloctane + 4-methyloctane	5.1	14.0	18.7	8.9	1.5	1.6	3.1	3.1	3.1
2,3-dimethylheptane	0.3	0.6	1.4	0.3	-	-	0.1	0.1	0.1
2-methyl 3-ethylhexane	0.04	0.12	0.4	-	-	-	0.10	0.10	0.10
2,5-dimethylheptane	1.0	1.5	4.2	0.6	-	0.04	0.66	0.66	0.66
C-9 isoparaffins (not mono-alkylisomers)	1.8	2.9	8.5	0.7	-	0.04	0.4	0.4	0.4
C-9 isoparaffins (not mono- or dialkylisomers)	0.1	0.6	0.6	1.6	-	0.3	0.9	0.9	0.9
normal nonane	80.2	40.0	12.3	35.0	41.1	34.0	25.2	25.2	25.2
fraction boiling over 152°C	-	-	-	-	-	-	0.9	0.9	0.9

+) contaminated with C-9 olefins at low concentrations

++) identification not certain

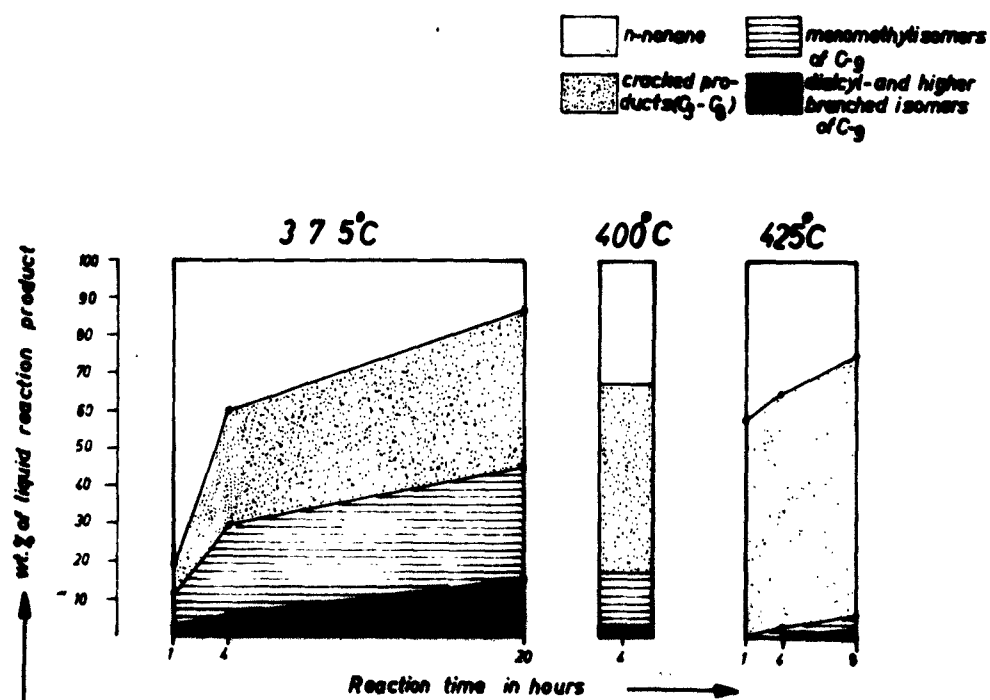


Fig. 15 Composition of the reaction products

Yields of C-9 isomers and cracked products ( $C_3-C_8$ ) are plotted in Fig. 15 (page 38) against the reaction time.

A temperature of 350°C was too low for the isomerization of normal nonane. The largest yield of C-9 isomers was obtained at a reaction temperature of 375°C and at a reaction time of 20 hours (apprx. 45 wt. % of the liquid reaction product).

Raising the reaction temperature from 375°C to 425°C decreased the yield of C-9 isomers rapidly

E.g. after a reaction time of four hours at 400°C apprx. 17 wt. % and at 425°C apprx. 3 wt. %. An increase in the reaction time at 375°C from 1 h to 20 hours increased the amount of both cracked products ( $C_3-C_8$ ) and C-9 branched isomers.

In the branched isomers of the C-9 fraction monomethyl ones represented the largest portion (over 65 wt. %). At a reaction temperature of 375°C the distribution of isomers in the C-4, C-5 and C-6 fractions of the cracked products was different than that at a reaction temperature of 425°C. At 375°C relatively more branched isomers in the corresponding fractions were obtained than at 425°C. At 425°C the n-compounds predominated.

### 5. Summary

A reaction temperature of 350°C was too low to initiate the isomerization of normal nonane. In the case of batch operations the largest yield of C-9 branched isomers was obtained by using long reaction times (20 h) at relatively low temperatures (375°C). In the case of continuous operations the highest yield was obtained only at higher temperatures (425°C) on account of the short contact time (10 sec.). Longer contact times at this temperature or higher reaction temperatures affected particularly the formation of cracked products.

From the branched isomers in the C-9 fraction monomethyl ones represented the largest portion (over 65 wt. %). In the case of continuous operations the ratio of dialkyl and higher branched isomers to monomethylisomers of C-9 increased with the conversion of the normal nonane. A similar effect was found by using normal hexane as feed, e. g. at high reaction temperatures (over 400°C) where high conversions were obtained was the ratio of dimethylisomers to monomethylisomers greater than at lower conversions under similar isomer-yield <sup>4)</sup>.

This is an indication of the high activation energy being required for the formation of the dialkyl and higher branched isomers. Monomethylisomers are formed, on the other hand, very easily.

In a reaction product the presence of the following individual branched isomers of C-9 was confirmed:

2-methyl-	2, 3 dimethyl
3-methyl-	2-methyl 3 ethyl-
4-methyl-	2, 5 dimethyl-

For the portion of C-9 isomers which have not been identified with certainty further analytical work is necessary. Attempts to obtain better resolution of peaks by gaschromatography and comparison of spectres of collected fractions with spectres of known compounds obtained with our Atlas-CH<sub>3</sub>-mass spectrometer gives the possibility for the identification of the yet unidentified hydrocarbons.

## References

- 1) R.L. Martin and J. C. Winters      Anal. Chemistry, vol. 31, p. 1954-80  
(1959)
- 2) A. G. Polgar, I. J. Holst and      Anal. Chemistry, p. 1226-33 (1962)  
Sigurd Groennings
- 3) L. P. Lindeman and J. L. Annis      Anal. Chemistry, vol. 32, p. 1742-9  
(1960)
- 4) M. Hartwig      Thesis, Karlsruhe 1962, p. 58

**End of report**

Summary of personnel utilized during the reporting period together with a summary of administrative actions, such as changes in research policies by the Contractor, etc.

The following staff members of the Engler-Bunte-Institute have been employed for the performance of the contract work.

1. Influence of Palladium content on the activity and selectivity of catalysts by the isomerization of n-hexane. Dr. M. Hartwig and one laboratory assistant. Full time over about 2 months.
2. Catalytic  
Isomerization and Hydrocracking of a soft paraffin wax.  
The experimental runs of this work had been conducted by Dr. N. Dengler and one lab. assistant. The analyses of reaction products by Dr. D. Kioussis. Full time over about 2 months.
3. Catalytic isomerization of n-nonane at batch operations and preparation of catalysts. Dr. A. Dawallu and one lab. assistant. Full time over a period of 3 months.
4. Catalytic isomerization of n-nonane at continuous operations - Dr. D. Kioussis and one lab. assistant. Full time over a period of 1 month.
5. Gas chromatography of branched isomers of C-9. (Determination of retention volumes of pure compounds; chromatographic analysis of a reaction product). Dr. D. Kioussis and one lab. assistant.  
Full time over a period of 3 months.
6. Mass spectroscopy analysis of a reaction product - Dipl. Phys. A. Herlan with two lab. assistants. Full time over a period of 1 month.
7. Work shop assistance was given by a number of mechanics under the supervision of Meister Bossert.

Supervision of the work:

Prof. Dr. H. Pichler

Typing: Miss v. Huene